mmol, 12.8%), biphenyl (0.6 mmol, 22.2%), 2-iodobiphenyl (0.07 mmol, 2.55%), 2,2′-diiodobiphenyl (0.5 mmol, 1.8%), 2-iodo-*o*-terphenyl (0.125 mmol, 4.25%), and small amounts of unidentified high-boiling products.

B. With Carbon Tetrachloride.—A yellow suspension of 0.86 (2.24 mmol) of 2 in 30 ml of carbon tetrachloride was stirred under Ar at room temperature in the dark for 6 hr. The white precipitate was collected, washed with carbon tetrachloride, and dried to give 0.563 g (1.8 mmol, 80%) of dibenziodolium chloride, mp 295° dec. The mother liquor was shown by peak enhancement with authentic samples to be a complex mixture of chlorobenzene, iodobenzene, benzotrichloride, biphenyl, 2-iodobiphenyl, 2-chloro-2′-iodobiphenyl, 2,2′-diiodobiphenyl, and traces of unidentified high-boiling products.

C. With Methyl Iodide.—A suspension of 1 g (2.08 mmol) of 2 in 50 ml of methyl iodide was stirred for 12 hr to yield 0.83 g (1.97 mmol, 70%) of dibenziodolium iodide, mp 220° dec. In the complex organic phase, benzene, toluene, iodobenzene, biphenyl, 2-iodobiphenyl, and 2,2′-diiodobiphenyl have been identified.

Cleavage of 5-Aryl-5*H*-dibenziodole with Hydrogen Chloride.—5-(*p*-Tolyl)-, 5-(*p*-chlorophenyl)-, 5-(*m*-chlorophenyl)-, and 5-(1-naphthyl)-5*H*-dibenziodole have been cleaved by benzoic acid and by hydrogen chloride in tetrahydrofuran. The mixtures of iodonium salts formed were all precipitated as iodides and analyzed as described previously.

Iodonium iodides obtained from 5-(*p*-tolyl)-5*H*-dibenzoidole decomposed to 4-iodotoluene (48%), 2-iodobiphenyl (45%), and 2,2′-diiodobiphenyl (52%). From 5-(1-naphthyl)-5*H*-dibenziodole, the iodides were pyrolyzed to 1-iodonaphthalene (23.8%), 2-iodobiphenyl (21.0%), and 2,2′-diiodobiphenyl (76.3%). 5-(*p*-Chlorophenyl)- and 5-(*m*-chlorophenyl)-5*H*-dibenziodole were cleaved by hydrogen chloride to form pure dibenziodolium chloride and with benzoic acid to give pure dibenziodolium benzoate.

Registry No.—2, 32174-73-5; 3, 32174-74-6; 4, 32174-75-7; 5, 32174-76-8; 6, 32174-77-9; 2-biphenylylphenyliodonium iodide, 32174-78-0; 2-biphenylylphenyliodonium fluoroborate, 32174-79-1; dibenziodolium fluoroborate, 18116-06-8; dibenziodolium methanesulfonate, 6478-21-8; 2-iodo-2′-biphenylylphenyliodonium iodide, 32174-81-5; dibenziodolium chloride, 4673-26-1; dibenziodolium iodide, 1010-76-0.

Transannular Interactions of the Silyl Center with Distant Keto Groups in the Mass Spectra of Medium-Sized Organosilicon Heterocycles. Improved Synthetic Routes to Six-, Seven-, and Eight-Membered Silicon Ring Systems

WILLIAM P. WEBER,* RAYMOND A. FELIX,[1] AND ALVIN K. WILLARD

Department of Chemistry, University of Southern California, University Park, Los Angeles, California 90007

HEINZ G. BOETTGER

Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109

Received June 1, 1971

The mass spectra of 4,4-dimethylsilacyclohexanone (I), 4,4-dimethylsilacycloheptanone (II), and 5,5-dimethylsilacyclooctanone (III) are discussed. I was prepared by a modified Dieckmann cyclization. II and III were prepared by use of a modified acyloin reaction. Significantly improved yields over previous synthetic routes were obtained.

Only a limited amount of work has been done so far on the mass spectra of functionally substituted organosilicon compounds. Significant differences from the behavior of analogous organic molecules in which silicon is replaced by carbon have been observed. These differences may arise due to strong interaction of the silyl center with electron-rich functional groups. Such interaction often leads to rearranged ions, in which the silyl center and the previously distant electron-rich functional group become directly bonded.[2,3] Two major types of rearrangements involving silyl centers have been observed. The first involves the direct transfer of an intact trimethylsilyl group from one part of the ion to another with concurrent fragmentation in a manner similar to certain types of specific hydrogen migrations frequently observed in mass spectrometry.[3,4] The second involves interaction of a siliconium ion center formed by loss of a methyl group from the quaternary silyl center with a distant electron-rich center in the molecule.[3]

We were interested in the mass spectral behavior of medium-sized organosilicon heterocyclic ketones, since it is well known that strong transannular interactions often play a dominant role in the carbonium ion chemistry of analogous medium-sized organic compounds.[5-7] We propose to discuss the mass spectra of three compounds in which transannular interaction of a silyl center with a remote keto functionality appears to play a dominant role. The compounds are 4,4-dimethylsilacyclohexanone (I),[8] 4,4-dimethylsilacycloheptanone (II),[9] and 5,5-dimethylsilacyclooctanone (III).[9]

Most of the major ions in the mass spectrum of I are probably formed by interaction of the silyl center with the carbonyl functionality. The fragmentation pattern of I is outlined in Figure 1. Metastable peaks at appropriate masses $m^* = (m_2)^2/m_1$ were observed for all fragmentation rearrangement processes discussed (see Table I).

The peak at mass 142 is the parent ion. Loss of a methyl radical from the parent leads to a siliconium ion at mass 127. Cleavage at a quaternary silyl center

---

[1] National Science Foundation Graduate Trainee, 1970–1971.

[2] W. P. Weber, R. A. Felix, and A. K. Willard, *J. Amer. Chem. Soc.*, **91**, 6544 (1969).

[3] W. P. Weber, R. A. Felix, and A. K. Willard, *ibid.*, **92**, 1420 (1970).

[4] G. H. Draffan, R. N. Stillwell, and J. A. McCloskey, *Org. Mass Spectrom.*, **1**, 669 (1968).

[5] V. Prelog, *Rec. Chem. Progr.*, **18**, 247 (1957).

[6] V. Prelog and J. G. Traynham in "Molecular Rearrangements," P. de Mayo, Ed., Interscience, New York, N. Y., 1963, p 593.

[7] A. C. Cope, M. M. Martin, and M. A. McKerray, *Quart. Rev., Chem. Soc.*, **20**, 119 (1966).

[8] R. A. Benkeser and E. W. Bennett, *J. Amer. Chem. Soc.*, **80**, 5414 (1958).

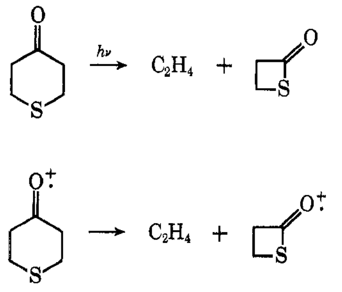
[9] R. A. Benkeser and R. F. Cunico, *J. Org. Chem.*, **32**, 395 (1967).

TABLE I

METASTABLE IONS OBSERVED

Possible process	Mass of metastable ion
4,4-Dimethylsilacyclohexanone	
142 → 127	113.6
142 → 114	91.5
114 → 99	85.9
127 → 99	77.2
114 → 86	64.8
4,4-Dimethylsilacycloheptanone	
156 → 141	127.5
156 → 128	105
128 → 113	99.5
141 → 113	90.5
5,5-Dimethylsilacyclooctanone	
170 → 155	141.4
170 → 142	118.6
142 → 127	113.6
155 → 127	104
142 → 114	91.5
114 → 99	85.9
127 → 99	77.2

is a favored process.[10,11] The parent ion also fragments by loss of C_2H_4 to yield an ion of mass 114. Deuterium labeling indicates specific loss of ethylene. The four hydrogens α to the carbonyl group were exchanged by base-catalyzed equilibration of I with D_2O. In the mass spectrum of I-d_4, the parent loses 30, *i.e.*, $C_2H_2D_2$, rather than 28, C_2H_4. A structure for this ion consistent with this result is the 1,1-dimethylsilacyclobutan-2-one cation radical. By analogy, Berchtold has reported that photolysis of the analogous γ-keto sulfide yields thiacyclobutan-2-one. A prominent ion formed by loss of C_2H_4 is also observed in the mass spectrum of this compound (eq 1).[12]



(1)

Loss of a methyl radical from the ion of mass 114 leads to an ion of mass 99. This α-keto siliconium ion is also formed by rearrangement of the mass 127 ion with specific loss of C_2H_4. Both the high resolution data and the mass spectrum of I-d_4 are consistent with these conclusions. Finally, the ion at mass 86 is formed by loss of carbon monoxide from the ion of mass 114 (see Tables II and III).

Clearly, the mass spectrum of 4,4-dimethylsilacyclohexanone is very different from that of cyclohexanone where major fragmentation processes are controlled by the initial cleavage α to the carbonyl group.[13,14]

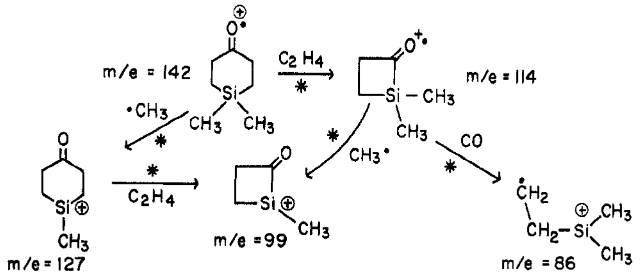


Figure 1.—Mass spectral fragmentation scheme for 4,4-dimethylsilacyclohexanone (*, metastable ion observed).

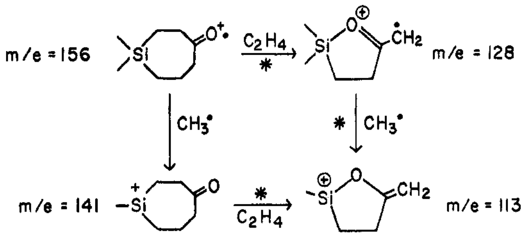


Figure 2.—Mass spectral fragmentation scheme for 4,4-dimethylsilacycloheptanone (*, metastable ion observed).

The mass spectrum of II (Table IV) is dominated by ions which may be formed by transannular interaction of the silyl center with the keto group. The fragmentation pattern of II is outlined in Figure 2. Metastable peaks were observed for all fragmentation–rearrangement processes discussed (see Table I). Loss of a methyl group from the silyl center of the parent ion at mass 156 leads to the expected siliconium ion at mass 141. The parent ion also fragments by loss of C_2H_4 to yield an ion of mass 128. Evidence for the specific loss of C_2H_4 was obtained by deuterium labeling. Exchange of the four hydrogens α to the keto group by base-catalyzed equilibration in D_2O leads to II-d_4. All four deuterium atoms are retained in the (parent − C_2H_4)$\cdot^+$ ion. Evidence that the P − 28 ion did not involve loss of carbon monoxide was obtained from high-resolution mass spectrometry (see Table V). Hence the P − 28 ion is probably formed by an intramolecular rearrangement in which the silyl center interacts with the positively charged carbonyl group with simultaneous loss of C_2H_4 specifically from the C_5–C_6 carbons of the three-carbon methylene bridge.[3]

Loss of a methyl radical from this ion of mass 128 leads to a siliconium ion of mass 113. This ion is also formed from the ion of mass 141, by loss of C_2H_4. In this case, the siliconium ion center interacts with the oxygen of the carbonyl group with simultaneous loss of C_2H_4. The spectrum of II-d_4 proves that C_2H_4 is specifically lost from C_5–C_6.

A note of caution must be sounded. In mass spectrometry one never absolutely knows the structure of an ion The transannular formation of an Si–O bond as shown in Figure 2 provides an economical explanation of the data consistent with the high silicon–oxygen bond strength.

A similar silyl-McLafferty rearrangement (eq 2) is observed to be a dominant fragmentation pathway in the mass spectrum of 5-trimethylsilylpentan-2-one (see Table VI).

---

(10) N. Ya. Cherynak, *et al.*, *Zh. Obshch. Khim.*, **36**, 89 (1966).

(11) N. Ya. Chernyak, *et al.*, *ibid.*, **36**, 96 (1966).

(12) P. Y. Johnson and G. A. Berchtold, *J. Org. Chem.*, **35**, 584 (1970).

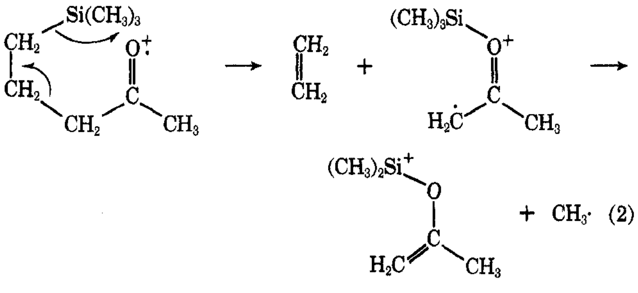
(13) D. H. Williams, H. Budzikiewicz, Z. Pelah, and C. Djerassi, *Montash. Chem.*, **95**, 166 (1964).

(14) J. Seibl and T. Gaumann, *Helv. Chim. Acta*, **46**, 2857 (1963).

TABLE II

MASS SPECTRUM OF 4,4-DIMETHYLSILACYCLOHEXANONE

Mass m/e	(I) 70 eV	(I) 20 eV	(I-d_4) 70 eV	(I-d_4) 20 eV	Mass m/e	(I) 70 eV	(I) 20 eV	(I-d_4) 70 eV	(I-d_4) 20 eV
39	2.5				97	1.5			
					98			0.25	
41	2.5				99	16.0	27.2	1.1	0.5
42	8.0		6.0		100	1.0	2.6	4.3	8.6
43	51.0		36.0		101	0.5	0.9	10.0	25.3
44	7.0		8.3		102			2.3	3.8
45	14.0		7.0		103			1.2	1.6
46	0.5		5.0		104			0.3	
47	1.5		1.0		105			0.3	
53	5.5		2.5		109	0.5			
54	1.5		2.0		110				
55	11.5		4.5		111	0.8		0.3	
56	2.5		6.0		112			0.5	
57	4.5		4.0		113	5.5	44.0	0.8	4.8
58	100.0	1.7	100.0	2.7	114	12.0	100.0	3.5	42.5
59	32.5		17.3	0.5	115	1.8	12.9	3.5	44.7
60	6.0		14.7		116	0.5	3.4	8.0	100.0
61	10.0		5.0		117	0.3		0.5	13.5
62			5.4		118			0.5	4.3
63			2.0		119				
66	0.5								
67	4.5				125	0.8	0.4		
68	0.5				126	0.3	0.4		
69	1.0		0.5		127	3.8	22.0	0.3	
70	1.5		2.0		128	0.5	2.6	0.5	2.7
71	7.5		2.0		129	0.3	0.9	0.5	6.5
72	1.5		3.5		130			1.3	11.8
73	1.0		4.5		131			2.0	14.0
74			0.5		132			0.3	1.6
75	8.5	6.5	4.0	4.3	133			0.3	1.6
76	0.5	0.4	3.5	6.5	134			0.3	0.5
77				0.5					
					141	2.8	16.4		
85	5.0		0.5		142	8.5	65.9		0.5
86	34.5	62.1	2.0	1.6	143	1.5	11.2	0.5	4.3
87	10.5	18.5	9.3	22.1	144	0.5	3.0	1.8	18.8
88	2.0	3.9	28.5	86.0	145			3.5	45.2
89		0.4	5.0	14.0	146			5.3	72.6
90			4.0	13.5	147			0.8	10.8
					148			0.3	2.7


(2)

The mass spectrum of III is also dominated by ions which probably arise by transannular interactions of the silyl center and the keto group. The fragmentation pattern of III is outlined in Figure 3. Metastable peaks were observed for all pathways discussed (see Table I). Loss of a methyl radical from the silyl center of the parent ion at mass 170 leads to a siliconium ion of mass 155. The parent ion also fragments by specific loss of C_2H_4 to yield an ion of mass 142. The four hydrogens α to the carbonyl group were exchanged by base-catalyzed equilibration with D_2O. The (parent − C_2H_4)$\cdot^+$ ion of III-d_4 retained all the deuterium. This demonstrates that the fragmentation process is similar to that observed in II. Loss of a methyl radical from this ion of mass 142 leads to a

TABLE III

HIGH-RESOLUTION MASS SPECTRAL DATA AT 70 EV FOR 4,4-DIMETHYLSILACYCLOHEXANONE

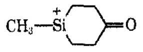
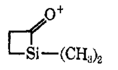
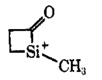
Elemental composition	Calcd mass	Obsd mass	Possible structure of ion
$C_7H_{14}SiO$	142.08139	142.0836	Parent
$C_7H_{13}SiO$	141.07356	141.0728	P − 1
$C_6H_{11}SiO$	127.05791	127.0573	
$C_5H_{10}SiO$	114.05009	114.0514	
C_5H_9SiO	113.04226	113.0407	
C_4H_7SiO	99.02662	99.0245	
$C_4H_{11}Si$	87.06300	87.0599	$(CH_3)_2—\overset{+}{Si}—CH_2CH_3$
$C_4H_{10}Si$	86.05518	86.0558	$(CH_3)_2\overset{+}{Si}—CH_2\dot{C}H_2$

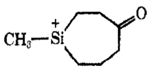
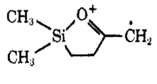
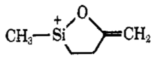
Table IV

Mass Spectrum of 4,4-Dimethylsilacycloheptanone

Mass m/e	(II) 70 eV	(II) 20 eV	(II-d_4) 70 eV	(II-d_4) 20 eV
55			15	
56			11	
57			16	
58	9		55	
59	16		57	
60			23	
61	7		12	
62			16	
63			8	
64			1	
65	3		1	
69				
70			7	
71	5		8	1
72	43	5	100	
73	4	1	35	1
74			65	1
75	27	4	29	1
76			38	
77	5		6	
78			2	
81			1	
82			1	
83			2	
84			2	
85	14		6	
86	5	1	12	
87	3		29	
88			13	
89			6	
95	6			
99	9	2	2	
100	7	6	6	1
101	4	1	6	1
102			10	6
103			3	1
104			2	
113	100	38	2	1
114	11	4	8	7
115	4	2	14	10
116		1	35	12
117			83	24
118			9	3
119			3	1
126				
127	22	18	1	
128	76	100	5	16
129	8	13	3	6
130	3	4	6	13
131			19	53
132			38	100
133			5	14
134			2	5
139	1			
140				
141	18	15		
142	2	2		1
143		1	1	4
144			3	9
145			4	12
146			1	2
155	3	1		
156	16	10		
157	2	1		
158			1	2
159			2	6
160			4	11
161			1	2

Table V

High-Resolution Mass Spectral Data at 70 eV for 4,4-Dimethylsilacycloheptanone

Elemental composition	Calcd mass	Obsd mass	Possible structure of ion
$C_8H_{16}SiO$	156.09704	156.0950	Parent
$C_7H_{13}SiO$	141.07356	141.0721	
$C_6H_{12}SiO$	128.06574	128.0697	
$C_6H_{11}SiO$	127.05791	127.0612	
C_5H_9SiO	113.04226	113.0457	

siliconium ion of mass 127. This ion is also formed by interaction of the siliconium ion center of the mass 155 ion with the carbonyl functionality with simultaneous specific loss of C_2H_4 from C_3–C_4 of the three-carbon methylene bridge. The ion of mass 142 fragments further by specific loss of C_2H_4 to yield an ion of mass 114. All four deuterium atoms of III-d_4 are retained in this ion as is required by the proposed mechanism.

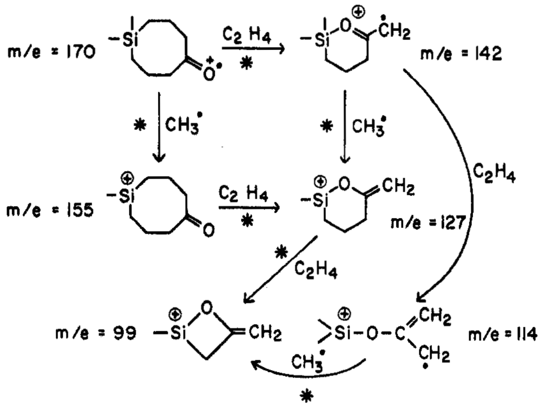


Figure 3.—Mass spectral fragmentation scheme for 5,5-dimethylsilacyclooctanone (*, metastable ion observed).

Loss of a methyl group from the silyl center of the mass 114 ion leads to an ion of mass 99. The ion of mass 127 also specifically loses C_2H_4 to yield the ion of mass 99. However, the spectrum of III-d_4 indicates

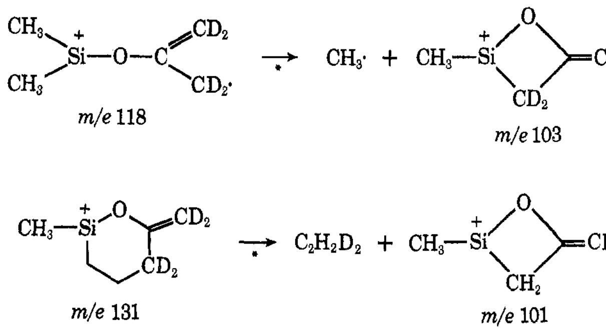
TABLE VI

5-TRIMETHYLSILYLPENTAN-2-ONE

Mass *m/e*	70 eV	20 eV	d_5 70 eV	d_5 20 eV
67	1.7			
68				
69	1.1			
70	1.7		3.5	
71	2.8		5.0	
72	17.9		22.3	
73	81.6	4.9	100.0	5.6
74	7.8		16.1	
75	76.0	25.8	26.2	3.5
76	5.6	1.5	65.3	11.7
77	2.2	0.5	13.8	17.7
78			6.9	11.2
79			1.2	3.0
85	2.8		1.9	
99	2.8			
100			1.5	
101			1.2	
115	100.0	66.3		
116	9.5	6.3		
117	2.8	2.0	6.2	7.6
118			24.6	26.9
119			64.2	46.1
120			57.3	34.0
121			7.3	4.1
122			1.9	
130	33.5	100.0		
131	3.4	11.2		
132	0.6	3.4		3.0
133			5.8	27.4
134			18.5	91.9
135			21.9	100.0
136			2.7	13.7
137				3.0
143	14.5	42.0		
144	1.1	4.9		
145	0.5	1.5		1.5
146			2.7	12.7
147			8.8	41.1
148			9.6	44.2
149			1.2	6.1
150				1.0

that these processes are complicated. In addition to an ion at mass 103, there is also observed a second peak of almost equal intensity at mass 101. It appears that the mass 103 ion is formed by loss of a methyl radical specifically from the mass 118 ion. A metastable peak at mass 89.9 = $(103)^2/118$ is observed. On the other hand, it appears that the mass 101 ion is formed by specific loss of $C_2H_2D_2$ from the mass 131 ion. In support of this a metastable peak is observed at 77.8 = $(101)^2/131$. No evidence in the form of metastable peaks indicates that the mass 118 ion rearranges to the mass 101 or that the mass 131 rearranges to the mass 103 ions. However, it is possible that both of these additional processes could be occurring (eq 3) (see Tables VII and VIII).

Again a final note of caution must be sounded. The structures of ions proposed are consistent with the mass spectral data but cannot be absolutely known by present methods.



(3)

In all the compounds discussed transannular interactions of the silyl center with the electron-rich carbonyl group dominate the spectra. The simplicity of the spectra supports the view that these interactions are powerful enough to suppress the usual complex fragmentation patterns of cyclic ketones.[13-15]

Synthesis.—All of the compounds have been previously reported by Benkeser.[8,9] However, our synthetic routes lead to improved overall yields.

Our route to I began with the preparation of dimethyldiallylsilane[16] by the *in situ* trapping of allyl Grignard by dimethyldichlorosilane. Dimethyldiallylsilane was converted to dimethyldi(3-hydroxypropyl)silane by a hydroboration–oxidation sequence.[17-19] This reaction is highly specific due to the directive effect of the γ-silyl center. The diol can be oxidized to the expected diacid by Jones reagent;[20,21] however, the yield is only 55%.[8] After esterification with methanol–H_2SO_4, the diester, dimethyldi(2-carbomethoxyethyl)silane,[8] was cyclized to the basic six-membered ring skeleton by a modified Dieckmann reaction.[22] This is of interest since a carbon–silicon bond is considerably longer than a carbon–carbon single bond. For this reason, preparing a six-membered ring containing silicon may be like preparing an all-carbon seven-membered ring system.[23] To achieve reasonable yields, the enolate anion formed in the Dieckmann cyclization must be trapped by rapid addition of trimethylchlorosilane to yield the corresponding silyl enol ether.[22] This prevents the reverse reaction which occurs if quenching of the anion is slow as by addition of water. This silyl enol ether is refluxed overnight in aqueous methanolic HCl to effect hydrolysis of the trimethylsilyl protecting group and decarboxylation of the β-keto acid. The overall yield was 27%.

The basic seven-membered ring skeleton of II is formed by an acyloin reaction on dimethyldi(2-carbomethoxyethyl)silane.[9] We have used the modification of adding trimethylchlorosilane.[22,24] A large excess of sodium is thus no longer required. Further, the reaction conditions remain essentially neutral instead of becoming strongly basic due to the presence of alkoxides. This is particularly useful for organo-

---

[15] J. H. Benyon, R. A. Saunders, and A. E. Williams, *Appl. Spectrosc.*, **14**, 95 (1960).

[16] C. A. Burkhard, *J. Amer. Chem. Soc.*, **72**, 1078 (1950).

[17] (a) H. C. Brown, K. J. Murry, L. J. Murry, J. A. Snover, and G. Zweifel, *ibid.*, **82**, 4233 (1960). (b) H. C. Brown and B. C. Subba Rao, *ibid.*, **81**, 6428 (1959).

[18] D. Seyferth, H. Yamazaki, and Y. Sato, *Inorg. Chem.*, **2**, 734 (1963).

[19] J. L. Speier, *J. Amer. Chem. Soc.*, **74**, 1003 (1952).

[20] K. Boden, I. M. Heibron, E. R. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1943).

[21] A. Bowors, T. G. Halsall, E. R. H. Jones, and A. J. Lemin, *ibid.*, 2555 (1943).

[22] U. Schräpler and K. Rühlmann, *Chem. Ber.*, **97**, 1383 (1964).

[23] J. P. Schaefer and J. J. Bloomfield, "Organic Reactions," Vol. 15, Wiley, New York, N. Y., 1967.

[24] J. J. Bloomfield, *Tetrahedron Lett.*, 587, 591 (1968).

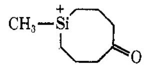
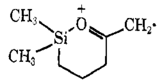
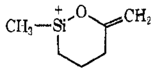
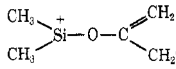
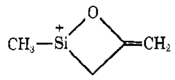
TABLE VII

MASS SPECTRUM OF 5,5-DIMETHYLSILACYCLOOCTANONE

Mass m/e	(III) 70 eV	(III-d_4) 70 eV	Mass m/e	(III) 70 eV	(III) 20 eV	(III-d_4) 70 eV	(III-d_4) 20 eV
50	6	2	109	2			
51	1	5	110				
52	1		111	3		1	
53	7	4	112			1	
54	2	2	113	6		2	
55	15	11	114	100	26	5	1
56	3	7	115	11	3	4	
57	10	9	116	4	1	7	2
58	15	18	117	1		33	12
59	42	38	118			100	31
60	5	12	119			12	4
61	24	11	120			4	1
62	2	11					
63	1	4	125	2		1	
64	1		126				
65	2	1	127	96	35	5	2
66	2	1	128	12	4	8	6
67	6	3	129	4	2	12	6
68	1	2	130			31	12
69	5	4	131			98	31
70	5	6	132			12	4
71	11	8	133			5	1
72	58	3					
73	11	12	141	1	1	2	2
74	4	35	142	58	100	2	3
75	39	19	143	8	11	1	1
76	3	25	144	2	3	4	7
77	3	5	145			22	36
78		2	146			62	100
79	1		147			8	14
80			148			3	4
81	5						
82			155	6	7		
83	4	2	156	1	1		
84	2	2	157			1	2
85	23	7	158			3	4
86	5	8	159			4	6
87	3	12	160				1
88		7	161				
89		3					
90		2	167				
			168				
95	1		169	0.3	0.3		
96	1		170	0.3	0.3		
97	3	1	171		0.1		
98	2	2	172				
99	60	6	173				
100	7	9	174				
101	2	27	175				
102		19					
103		32					
104		4					
105		1					

TABLE VIII

HIGH-RESOLUTION MASS SPECTRAL DATA AT 70 eV FOR 5,5-DIMETHYLSILACYCLOOCTANONE

Elemental composition	Calcd mass	Obsd mass	Possible structure of ion
$C_8H_{15}OSi$	155.08921	155.0870	
$C_7H_{14}OSi$	142.08139	142.0815	
$C_6H_{11}SiO$	127.05791	127.0585	
$C_5H_{10}OSi$	114.05009	114.0503	
C_4H_7OSi	99.02662	99.0291	
C_4H_9Si	85.04735	85.0456	$(CH_3)_2\overset{+}{Si}—CH{=}CH_2$
C_2H_7OSi	75.02662	75.0286	$(CH_3)_3—\overset{+}{Si}—OH$
C_3H_8Si	72.03953	72.0402	
C_2H_7Si	59.03170	59.0315	

silicon compounds, since alkoxides can cleave certain carbon–silicon bonds.[25] The product is not the acyloin but rather a bis-silyl enol ether. The bis-silyl enol ether is converted to the α-acetoxy ketone by hydrolysis in acetic acid–acetic anhydride.[26] The α-acetoxy ketone is reduced to the desired ketone by treatment with zinc dust in acetic acid.[27] The overall yield is 12%.

The basic eight-membered ring skeleton of 4,4-dimethylsilacyclooctanone and III was prepared by use of an acyloin reaction. This required preparation of a suitable precursor diester. The problem is basically one of connecting unsymmetrical groups to silicon. Our sequence starts with the bromination of trimethylchlorosilane to yield dimethylbromomethylchlorosilane.[28] Addition of allyl Grignard to this yields dimethylallylbromomethylsilane. This is expected, since a silicon–chlorine bond is much more reactive than a carbon–bromine bond. Dimethylallylbromomethylsilane was then converted to the corresponding Grignard reagent, to which was added allyl bromide. The product, dimethylallyl-3-butenylsilane, was converted to dimethyl(3-hydroxypropyl)(4-hydroxybutyl)silane by hydroboration–oxidation in excellent yield.[17] The diol was oxidized to the corresponding diacid by use of the Jones reagent.[20,21] The diacid was esterified with methanolic HCl to yield dimethyl(2-carbomethoxyethyl)(3-carbomethoxypropyl)silane. This was then cyclized to the basic eight-membered ring skeleton by use of the modified acyloin reaction.[22,24] The bis-silyl enol ether was hydrolyzed to the corresponding pair of isomeric α-acetoxy ketones as before.[26] They were not separated but were converted directly to the ketones by treatment with zinc dust in acetic acid.[27] The ketones were separated by gas chromatography. The overall yield was 3%.

The greater accessibility of these medium-sized organosilicon heterocycles opens the possibility of studying many types of transannular interactions in these systems.

Experimental Section

All reactions were carried out under a nitrogen atmosphere. All products were distilled through a 25-cm vacuum jacketed

---

[25] C. Eaborn, "Organosilicon Compounds," Butterworths, London, 1959, pp 129–140.

[26] K. Rühlmann, H. Seefluth, and H. Becker, *Chem. Ber.*, **100**, 3820 (1967).

[27] R. S. Rosenfeld and T. F. Gallagher, *J. Amer. Chem. Soc.*, **77**, 4367 (1955).

[28] J. L. Speier, *ibid.*, **73**, 826 (1951).

Vigreux column unless otherwise noted. All compounds were purified for mass spectral study by preparative gas chromatography on a 0.25 in. × 10 ft SE-30 column unless otherwise noted. Ir spectra were determined in CCl_4 solution on a Perkin-Elmer 337. Nmr spectra were run on a Varian HA-100 using 10% solutions in CCl_4. Chloroform or methylene chloride was used as internal standard. Microanalysis was done by Elek Microanalytical Laboratory.

Conditions in determining low-resolution mass spectra on a Hitachi RMU-6E instrument were source temperature 200°; all-glass inlet temperature 200°; ionizing voltage 70 and 20 eV; filament emission 70 μA; target current 50 μA. Comparisons were made between unlabeled compounds and labeled compounds at 20 eV under identical conditions.

Conditions used in determining high resolution spectra on the AEI MS-902 instrument were as follows. Exact mass determination of the composition of important ions were carried out at a resolution of at least 10,000 by peak matching with peaks of known mass of perfluorokerosene: ionizing voltage 70 eV; filament emission 480 μA; source temperature 150°.

Dimethyldiallylsilane was prepared by the *in situ* trapping of allylmagnesium bromide by dimethyldichlorosilane in THF. The product was distilled; a central fraction, bp 134°, was obtained in 94% yield.[16]

Dimethyldi(3-hydroxypropyl)silane was prepared by hydroboration-oxidation of dimethyldiallylsilane.[17] The diol was purified by distillation; a central fraction, bp 133–135° (1.5 mm), was obtained in 92% yield. Its physical properties were in agreement with literature values.[7,19] Nmr spectrum follows: s (6 H) δ 0.1; m (4 H) 0.4; m (4 H) 1.4, t (4 H) 3.4, J = 7 Hz; s(2 H), 3.6.

Dimethyl(2-carbomethoxyethyl)silane.—In a 5-l. flask equipped with a mechanical stirrer, a thermometer, and an addition funnel was placed 100 g (0.57 mol) of dimethyldi(3-hydroxypropyl)silane dissolved in 700 ml of reagent acetone. The flask was cooled to 0° in an ice–salt bath; 1.14 l. of Jones reagent[20,21] was then added at a rate such that the reaction temperature remained below 20°. The reaction mixture was then stirred for an additional 15 min. The organic layer was separated, and the aqueous layer was extracted with three 500-ml portions of ether. The combined organic layers were extracted with 20% sodium hydroxide until the extract was basic. This basic solution was then acidified and extracted with three 500-ml portions of ether. The ether extracts were dried over anhydrous $MgSO_4$ and filtered, and the solvent was removed by evaporation under reduced pressure. The crude diacid was then refluxed overnight with 600 ml of methanol containing 5 ml of concentrated H_2SO_4. The volume was then reduced to one-third by evaporation under reduced pressure; 500 ml of ether was added; and the organic layer was extracted twice with 100-ml portions of water followed by 100-ml portions of 10% sodium hydroxide until the extracts were basic. The organic layer was then dried over anhydrous $MgSO_4$ and filtered, and the solvent was removed by evaporation under reduced pressure. The residue was distilled, a fraction, bp 90–100° (0.3 mm), 70 g, was obtained, 53% yield. This diester had properties in agreement with reported values.[8]

1,1-Dimethyl-4-trimethylsiloxy-3-carbomethoxy-1-silacyclohexa-3-ene.—A 2-l., three-necked, round-bottom flask equipped with a mechanical stirrer, a pressure-equalizing addition funnel, and a reflux condenser was flamed out under nitrogen. In the flask was placed 24 g (1 mol) of NaH and 1 l. of dry toluene. The mixture was stirred at reflux while 54 g (0.23 mol) of dimethyldi(2-carbomethoxyethyl)silane was added over 4 hr. The reaction was then quenched by the addition of 66 g (0.6 mol) of trimethylchlorosilane.[22] The reaction mixture was then filtered and the solvents were removed by distillation at atmospheric pressure. The residue was distilled; a fraction, bp 80–85° (0.15 mm), 36 g (56% yield), was obtained. The ir had a C–C double bond stretch at 1600 cm^{-1} and a carbonyl band at 1710 cm^{-1}; nmr s (6 H) δ −0.15; s (9 H) −0.03; t (2 H) 0.50, J = 7 Hz; s (2 H) 1.27; t (2 H) 2.07; s (3 H) 3.39, J = 7 Hz. The exact mass of the parent ion was found to be 272.1222; calculated for $C_{12}H_{24}O_3Si_2$, 272.1257. The exact mass of the (P − CH_3) ion was found to be 257.0992; calculated for $C_{11}H_{21}O_3Si_2$, 257.1023.

4,4-Dimethylsilacyclohexanone.—A mixture of 30 ml of concentrated HCl, 300 ml of methanol, 100 ml of H_2O, and 33 g (0.12 mol) of 1,1-dimethyl-4-trimethylsiloxy-3-carbomethoxy-1-silacyclohexa-3-ene was stirred at reflux for 24 hr. The solution was then extracted with two 100-ml portions of ether. The organic layer was dried over anhydrous $MgSO_4$ and filtered and solvent was removed by evaporation under reduced pressure. The residue was then distilled; a fraction, bp 110° (25 mm), was collected, 17 g (95% yield). All properties were in agreement:[7] nmr spectrum s (6 H) δ 0.13; t (4 H) 0.88, J = 7.5 Hz; t (4 H) 2.40, J = 7.5 Hz.

1,1-Dimethyl-4,5-di(trimethylsiloxy)-1-silacyclohept-4-ene.—A 1-l., three-necked flask equipped with a high speed stirrer, pressure-equalizing addition funnel, and a reflux condenser was flamed out under nitrogen. In the flask was placed 16.0 g (0.7 g-atom) of sodium and 300 ml of dry toluene. After the toluene was heated to reflux, stirring was begun. To this Na dispersion was added a mixture of 90 ml of trimethylchlorosilane (0.7 mol) and 25.9 g of dimethyldi(2-carbomethoxyethyl)silane over several hours.[22,24] The reaction was stirred for 2 hr after the addition was complete. The mixture was then filtered. The solvent was removed by distillation at atmospheric pressure. The residue was then distilled, a fraction boiling at 90–100° (0.1 mm), 20 g, was obtained, 60% yield: nmr spectrum s (6 H) δ 0.0; s (18) 0.2; m (4 H) 0.6; m (4 H) 2.2. Its ir has a C–C double bond stretch at 1680 cm^{-1}. The mass spectrum of such bis-silyl enol ethers are quite interesting in that the parent ion carries a high portion of the total ion current. The exact mass of the parent ion was found at 316.1770 (calcd for $C_{14}H_{32}O_2Si_3$: 316.1701).

5,5-Dimethyl-2-acetoxy-5-silacycloheptanone.—A mixture of 13.0 g (41.2 mmol) of 1,1-dimethyl-4,5-di(trimethylsiloxy)-1-silacyclohepta-4-ene, 12 ml of glacial acetic acid, 12 ml of acetic anhydride, and 150 mg of sodium acetate[26] was stirred at reflux for 3 hr. After removal of 18 ml of solvent by distillation at atmospheric pressure, the residue was taken up in 50 ml of ether. The solution was extracted with 50 ml portions of water, followed by 20-ml portions of 10% sodium hydroxide solution until the extracts were basic. The organic layer was then dried over anhydrous $MgSO_4$ and filtered, and the solvents were removed by evaporation under reduced pressure. The residue was distilled; a central fraction, bp 80–85° (0.25 mm), 7 g, was collected, 80% yield. Its ir had two carbonyl bands at 1720 and 1740 cm^{-1}; nmr spectrum s (3 H), δ 0.8; s (3 H) 0.12; m (4 H) 0.8; m (2 H) 2.00; s (3 H) 2.07; m (2 H) 2.50; and m (1 H) 5.40. *Anal.* Calcd for $C_9H_{18}O_2Si$: C, 56.04; H, 8.45. Found: C, 55.69; H, 8.39.

4,4-Dimethylsilacycloheptanone.—In a 200-ml, three-necked round-bottom flask equipped with a Hirshberg mechanical stirrer and a reflux condenser was placed 7.8 g (36.5 mmol) of 5,5-dimethyl-2-acetoxy-5-silacycloheptanone dissolved in 100 ml of glacial acetic acid. The reaction mixture was heated to reflux, while 24 g (0.4 mol) of reagent zinc dust was added in several small batches over 4 hr.[27] The solution was then decanted from the solids, which were washed with 100 ml of ether. The organic layer was extracted with two 50-ml portions of water, and then with 20-ml portions of 10% NaOH until the aqueous extracts were basic. The organic layer was then dried over anhydrous $MgSO_4$ and filtered, and the solvent was removed by evaporation under reduced pressure. The residue was distilled. Two fraction were collected: the first, bp 115° (25 mm) (1.5 g), was largely the desired ketone; the second, bp 140° (25 mm) (4 g), was largely recovered α-acetoxy ketone. The yield of ketone based on converted α-acetoxy ketone is 50%. All physical properties were in agreement with those reported.[8]

Dimethylbromomethylchlorosilane was prepared by the bromination of trimethylchlorosilane following the method of Speier.[28] The product was purified by distillation. A central fraction, bp 134°, was collected: yield 50%; nmr spectrum s (6 H) δ 0.50; s (2 H) 2.35.

Dimethylallylbromomethylsilane was prepared by the addition of allylmagnesium bromide to dimethylbromomethylchlorosilane in ethyl ether. After work-up, the residue was distilled, and a fraction, bp 84–88° (25 mm), was collected, yield 65%. Its ir is characterized by a C–C double bond stretch at 1625 cm^{-1}; nmr spectrum s (6 H) δ 0.14; d (2 H) 1.64, J = 7 Hz; s (2 H) 2.43; a pair of multiplets (2 H) 4.80 and 4.92; and m (1 H) 5.77. *Anal.* Calcd for $C_6H_{13}BrSi$: C, 37.31; H, 6.78. Found: C, 37.16; H, 6.74.

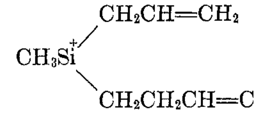
Dimethylallyl-3-butenylsilane.—A 1-l. three-necked flask equipped with a pressure-equalizing addition funnel, a reflux condenser, and a magnetic stirring bar was flamed out under nitrogen. In the flask was placed 200 ml of dry THF and 5.2 g (0.22 g-atom) of Mg turnings. To this was added 34.8 g (0.18 mol) of dimethylallylbromomethylsilane dropwise with stirring. When formation of the Grignard reagent was complete 36 g (0.3 mol) of allyl bromide was added. When the coupling reaction had ceased 100 ml of water was added. The layers were separated and the organic layer was washed with two 100-ml portions of water. The organic layer was then dried over anhydrous $MgSO_4$ and filtered, and the solvents were distilled at atmospheric pressure. The residue was distilled; a central fraction, bp 62–64° (25 mm), 20 g, was collected, 80% yield. Its ir is characterized by a C–C double bond stretch at 1630 cm^{-1}; nmr spectrum s (6 H) δ 0.0; m (2 H) 0.63; d (2 H) 1.50; m (2 H) 2.00, J = 8 Hz; m (4 H) 4.90; m (2 H) 5.70.

The mass spectrum of the compound is characterized by siliconium ions produced by fragmentation at the quaternary silyl center. High-resolution mass spectral data are shown below.

parent ion $\cdot^{+}$

Calcd for $C_9H_{18}Si$ 154.11777

Found 154.1226



$CH_3\overset{+}{Si}(CH_2CH{=}CH_2)(CH_2CH_2CH{=}CH_2)$

Calcd for $C_8H_{15}Si$ 139.09430

Found 139.0938

$(CH_3)_2\overset{+}{Si}CH_2CH_2CH{=}CH_2$

Calcd for $C_6H_{13}Si$ 113.07865

Found 113.0810

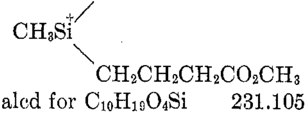
$(CH_3)_2\overset{+}{Si}CH_2CH{=}CH_2$

Calcd for $C_5H_{11}Si$ 99.0630

Found 99.0642

Dimethyl(3-hydroxypropyl)(4-hydroxybutyl)silane was prepared by the hydroboration and oxidation of dimethylallyl-3-butenylsilane in THF.[17,18] The residue was distilled, a central fraction, bp 145–150° (0.1 mm), was obtained in 90% yield. Its ir has a strong OH stretch at 3600–3200 cm^{-1}; nmr spectrum s (6 H) δ −0.1; m (4 H) 0.40; m (6 H) 1.40; m (4 H) 3.40; and a broad singlet at 3.70 (2 H). This last resonance disappeared after exchange with D_2O. The diol was converted to the corresponding diacetate by treatment with acetyl chloride in pyridine. This was done to have a volatile derivative which could be purified by gas chromatography. Its ir has a carbonyl stretch at 1740 cm^{-1}: nmr spectrum s (6 H) δ 0.0; m (4 H) 0.50; m (6 H) 1.55; s (6 H) 2.00; t (2 H) 3.94; J = 7 Hz; t (2 H) 4.00, J = 7 Hz. *Anal.* on diacetate. Calcd for $C_{13}H_{26}O_4Si$: C, 56.90; H, 9.59. Found: C, 57.05; H, 9.43.

Dimethyl (2-carbomethoxyethyl)(3-carbomethoxypropyl)silane was prepared by Jones oxidation[20,21] of dimethyl(3-hydroxypropyl)(4-hydroxybutyl)silane to the corresponding diacid followed by esterification with methanolic H_2SO_4. The procedure is the same as was used to prepare dimethyldi(2-carbomethoxyethyl)silane. The residue was distilled, a central fraction, bp 105° (0.2 mm), was collected in average yield (45%). The ir has a carbonyl stretch at 1745 cm^{-1}; nmr spectrum s (6 H) δ 0.00; m (4 H) 0.80; m (2 H) 1.60; m (4 H) 2.20; and s (6 H) at 3.70. Its mass spectrum is characterized by siliconium ions formed by fragmentation at the quaternary silyl center. The parent ion is quite small. The exact masses of the following three siliconium ions were determined.



$CH_3\overset{+}{Si}(CH_2CH_2CO_2CH_3)(CH_2CH_2CH_2CO_2CH_3)$

Calcd for $C_{10}H_{19}O_4Si$ 231.10525

Found 231.1019

$(CH_3)_2\overset{+}{Si}CH_2CH_2CH_2CO_2CH_3$

Calcd for $C_7H_{15}O_2Si$ 159.08413

Found 159.0830

$(CH_3)_2\overset{+}{Si}CH_2CH_2CO_2CH_3$

Calcd for $C_6H_{13}O_2Si$ 145.06848

Found 145.0667

1,1-Dimethyl-4,5-di(trimethylsiloxy)-1-silacycloocta-4-ene was prepared by an acyloin reaction of dimethyl(2-carbomethoxyethyl)(3-carbomethoxypropyl)silane. The same procedure was used to prepare the corresponding seven-membered ring compound.[22,24] The residue was distilled, a central fraction, bp 95° (0.1 mm), was collected, average yield 60%. The ir has a characteristic C–C double bond stretch at 1680 cm^{-1}; nmr s (6 H) δ 0.00; s (9 H) 0.18; s (9 H) 0.22; m (4 H) 0.85; m (2 H) 1.75; and m (4 H) 2.16. The mass spectrum of such bissilyl enol ethers are quite interesting in that the parent ion carries a quite high percentage of the total ion current. The exact mass of the parent ion was found to be 330.1928 (calculated for $C_{15}H_{34}O_2Si_3$, 330.1857).

5,5-Dimethyl-2-acetoxy-5-silacyclooctanone and 6,6-Dimethyl-2-acetoxy-6-silacyclooctanone.—A mixture of the two compounds was prepared by reaction of 1,1-dimethyl-4,5-di(trimethylsiloxy)-1-silacyclooct-4-ene with a mixture of glacial acetic acid and acetic anhydride by the same procedure used to prepare 2-acetoxy-5,5-dimethylsilacycloheptanone.[26] The residue was distilled; a fraction, bp 90° (0.1 mm), 13 g, was collected, 85% yield. Preparative gas chromatography served to purify the mixture, but not to separate the isomeric acetoxy ketones. The ir of the mixture was characterized by two carbonyl bands, one at 1720 and the other at 1745 cm^{-1}. *Anal.* Calcd for $C_{11}H_{20}O_3Si$: C, 57.85; H, 8.83. Found: C, 57.99; H, 8.80.

4,4-Dimethylsilacyclooctanone and 5,5-dimethylsilacyclooctanone were prepared by the reduction of the mixture of acetoxy ketones by Zn and acetic acid.[27] The procedure was the same as was used to prepare 4,4-dimethylsilacycloheptanone. The residue was distilled; a fracton, bp 115° (25 mm), was collected, yield 55%. The isomeric ketones were separated on a 0.25 in. × 15 ft TCEP column at 135°. The component with the shorter retention time (48 min) was the symmetrical ketone. The component with the longer retention time (55 min) was the unsymmetrical ketone. They were present in a ratio of 60:40 symmetrical to unsymmetrical.

Properties of 4,4-Dimethylsilacyclooctanone.—Its ir has a carbonyl band at 1710 cm^{-1}; nmr spectrum s (6 H) δ 0.00; m (2 H) 0.56; m (2 H) 1.00; m (4 H) 1.82; m (4 H) 2.40. The exact mass of the parent ion determined by peak matching. Calcd for $C_9H_{18}OSi$: 170.1122. Found: 170.1072.

Properties of 5,5-Dimethylsilacyclooctanone.—Its ir showed a carbonyl band at 1710 cm^{-1}; nmr spectrum s (6 H) δ −0.07; m (4 H) 0.68; m (4 H) 1.91; m (4 H) 2.34. For high-resolution mass spectral data, see Table VIII.

5-Trimethylsilylpentan-2-one was prepared following the procedures of Sommer.[29] Its ir was characterized by a carbonyl stretch at 1720 cm^{-1}. Its nmr spectrum showed s (9 H) δ 0.0; m (2 H) 0.5; m (2 H) 1.6; s (3 H), 2.1; t (2 H) 2.4, J = 6.8 Hz.

Deuterium Exchange.—The various ketones were deuterium labeled by the following procedure: 0.5 g of the desired ketone, 6 ml of D_2O (99.8% deuterium), 0.2 g of sodium carbonate, 15 ml of dioxane, and 5 ml of THF were placed in a small round-bottom flask equipped with a magnetic stirring bar and a reflux condenser. The reaction was stirred at reflux for 24 hr. The solution was then extracted with two 30-ml portions of pentane. The organic layer was then washed with two 10-ml portions of water, dried over anhydrous $MgSO_4$, and filtered, and finally the solvents were removed by evaporation under reduced pressure. Final purification was by preparative gas chromatography.

Deuterium content was determined at 20 eV using low-resolution mass spectral data. The analysis was complicated by a significant (P − 1) peak associated with the parent ion in the spectra of the unlabeled compounds. For this reason, the analysis was done using the (P − 15) peak due to cleavage of a methyl group from silicon which has no complicating (P − 15 − 1) ion associated with it.[30]

Deuterium contents determined were as follows: 4,4-dimethylsilacyclohexanone, d_4 38.7%, d_3 33.7%, d_2 19.2%, d_1 8.4%; 4,4-dimethylsilacycloheptanone, d_4 44.4%, d_3 35.2%, d_2 16.2%, d_1 4.2%; 5,5-dimethylsilacyclooctanone, d_4 48.9%, d_3 33.2%, d_2 17.9%; 5-trimethylsilylpentan-2-one, d_5 42.1%, d_4 42.8%, d_3 13.5%, d_2 1.6%.

Registry No.—I, 18276-42-1; II, 10325-26-5; III, 10325-31-2; 1,1-dimethyl-4-trimethylsiloxy-3-carbo-

---

(29) L. H. Sommer, F. P. Mackay, O. W. Steward, and P. G. Campbell, *J. Amer. Chem. Soc.*, **79**, 2764 (1967).

(30) K. Biemann, "Mass Spectrometry—Organic Chemical Applications," McGraw-Hill, New York, N. Y., 1962; see Chapter 5 for treatment of data for deuterium-labeled compounds.

methoxy-1-silacyclohexa-3-ene, 32297-02-2; 1,1-dimethyl-4,5-di(trimethylsiloxy)-1-silacyclohept-4-ene, 32297-03-3; 5,5-dimethyl-2-acetoxy-5-silacycloheptanone, 32297-04-4; dimethylbromomethylchlorosilane, 16532-02-8; dimethylallylbromomethylsilane, 32367-49-0; dimethylallyl-3-butenylsilane, 24171-43-5; dimethyl(3-hydroxypropyl)(4-hydroxybutyl)silane, 32367-50-3, 32367-51-4 (diacetate); dimethyl(2-carbomethoxyethyl)(3-carbomethoxypropyl)silane, 32367-52-5; 1,1-dimethyl-4,5-di(trimethylsiloxy)-1-silacyclocta-4-ene, 32296-53-0; 5,5-dimethyl-2-acetoxy-5-silacyclooctanone, 32296-54-1; 6,6-dimethyl-2-acetoxy-6-silacyclooctanone, 32296-55-2; 4,4-dimethylsilacyclooctanone, 32296-56-3; 5-trimethylsilylpentan-2-one, 17012-93-0.

Acknowledgments.—This work was supported in part by a Biomedical Sciences Support Grant RR-07012-04 from the National Institutes of Health. We also thank the Caltech President's Fund and NASA Contract NAS 7-100.

Reactions of 2-Methylchloroferrocene. Evidence for the Ferrocyne Intermediate[1]

J. W. HUFFMAN* AND J. F. COPE

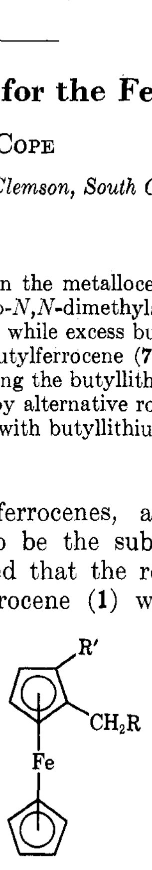
Department of Chemistry and Geology, Clemson University, Clemson, South Carolina 29631

Received May 27, 1971

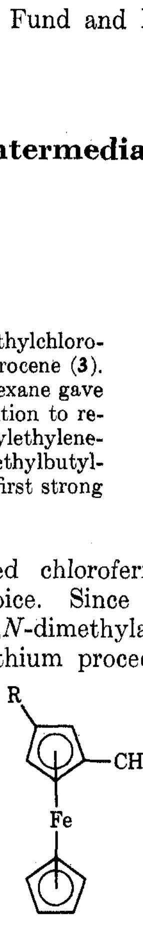
In an effort to investigate the possibility of aryne intermediates in the metallocene series, 2-methylchloroferrocene (2) was prepared by reduction of the methiodide of 2-chloro-*N*,*N*-dimethylaminomethylferrocene (3). Reaction of 2 with butyllithium in tetrahydrofuran gave α-lithiation, while excess butyllithium in hexane gave a mixture of approximately equal parts of 2-methyl- and 3-methylbutylferrocene (7 and 8) in addition to recovered 2 and methylferrocene (6). Similar results were obtained using the butyllithium–tetramethylethylenediamine complex. For reference samples, 7 and 8 were synthesized by alternative routes, and 1′-methylbutylferrocene (9) was also prepared. The results from the reaction of 2 with butyllithium provide the first strong evidence for an aryne intermediate in the ferrocene series.

Several years ago, in work carried out in these laboratories, reactions of chloroferrocene with butyllithium and butyllithium–lithium piperidide were carried out.[2] The products obtained in this study indicated that these reactions were probably proceeding *via* a ferrocyne intermediate, but alternative paths involving prior halogen–metal interconversion could not be excluded.[2] Following our earlier publication, there have been no additional studies on the intermediacy of arynes in the metallocene series, and the only related work appears to be the recent preparation and subsequent trapping of dehydrocyclopentadiene[3] and the selective α-lithiation experiments carried out on haloferrocenes by Hedberg and Rosenberg.[4]

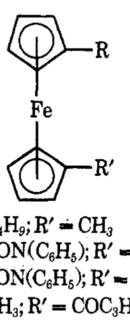
In order to establish whether the reaction of chloroferrocene with *n*-butyllithium to give butylferrocene was an example of an aryne reaction or simply Wurtz–Fittig coupling, a substrate which would give an unsymmetrical aryne was needed. The classical work in the benzene series was carried out using such compounds as *o*-bromoanisole and the halotoluenes,[5] and by analogy it appeared that the reaction of a 2- or 3-substituted chloroferrocene with butyllithium should serve to either establish or refute the existence of the ferrocyne intermediate. In view of the limited synthetic methods available for preparing 1,3-disubstituted ferrocenes, a 2-substituted chloroferrocene seemed to be the substrate of choice. Since it has been noted that the reaction of *N*,*N*-dimethylaminomethylferrocene (1) with *n*-butyllithium proceeds to give almost exclusively lithiation at the 2 position[6] and since the replacement of the dimethylamino group by hydrogen was quite feasible, 2-methylchloroferrocene (2) was chosen as the subject of our study. Initially



1, $R = N(CH_3)_2$; $R' = H$
2, $R = H$; $R' = Cl$
3, $R = N(CH_3)_2$; $R' = Cl$
4, $R = N(CH_3)_2$; $R' = B(OH)_2$
5, $R = N(CH_3)_3{}^+I^-$; $R = Cl$
6, $R = R' = H$
7, $R = H$; $R' = C_4H_9$
12, $R = N(CH_3)_2$; $R' = CH = CHC_2H_5$
13, $R = H$; $R' = COC_3H_7$



8, $R = C_4H_9$
14, $R = COC_3H_7$



9, $R = C_4H_9$; $R' = CH_3$
10, $R = CON(C_6H_5)$; $R' = H$
11, $R = CON(C_6H_5)$; $R' = COC_3H_7$
15, $R = CH_3$; $R' = COC_3H_7$

---

[1] (a) Abstracted from the Ph.D. Dissertation of J. F. Cope, Clemson University, May 1971; (b) supported in part by Career Development Award GM-5433 from the National Institutes of Health.

[2] J. W. Huffman, L. H. Keith, and R. L. Asbury, *J. Org. Chem.*, **30**, 1600 (1965).

[3] J. C. Martin and D. R. Block, *J. Amer. Chem. Soc.*, **93**, 451 (1971).

[4] (a) F. L. Hedberg and H. Rosenberg, *Tetrahedron Lett.*, 4011 (1969). (b) A. N. Nesmeyanov, B. A. Sazonova, and N. S. Sazonova, *Dokl. Akad. Nauk SSSR*, **176**, 598 (1967), reported the preparation and thermal decomposition of 2-chloroferrocenylsilver, but observed no products indicative of an aryne reaction.

[5] (a) T. L. Gilchrist and C. W. Rees, "Carbenes, Nitrenes and Arynes," Appleton–Century–Crofts, New York, N. Y., 1969, pp 42–54 and 103–119, (b) H. Heaney, *Chem. Rev.*, **62**, 81 (1962), and (c) R. Huisgen in "Organometallic Chemistry," H. Zeiss, Ed., Reinhold, New York, N. Y., 1960, pp 36–88, have all reviewed the work which establishes the fact that arynes are intermediates in the reactions of halobenzenes with strong bases.

[6] D. W. Slocum, B. W. Rockett, and C. R. Hauser, *J. Amer. Chem. Soc.*, **87**, 1241 (1965).